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(71)Applicant : KAWATA MFG CO LTD
OSAKA PREFECTURE

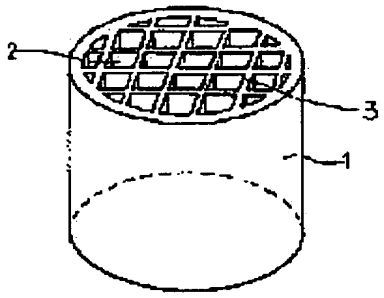
(72)Inventor : MIYAMOTO DAIKI
OTA MICHINOSUKE
ISHIKAWA KANZO
SUKETA YOSHIHIKO
KAJI YASUNARI

(54) FIBER REINFORCED HONEYCOMB CERAMIC BODY AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a fiber reinforced honeycomb ceramic body hardly causing brittle fracture by molding and firing a compsn. contg. ceramic powder, inorg. fibers and an inorg. substance having binding property or further contg. an org. binder having plasticity.

CONSTITUTION: Ceramic powder such as alumina, spinel or silicon carbide powder, inorg. fibers such as ceramic, metal or carbon fibers and an inorg. substance having binding property such as colloidal silica, sepiolite or an alumina sol are prepd. and a ceramic-contg. compsn. is obtd. by using these starting materials or further using an org. binder such as PVA or methylcellulose. This compsn. having satisfactory extrusion moldability is extrusion-molded into a honeycomb shape with holes 2 having a square cross section formed by partition walls 3. The resulting molding is dried and fired at a temp. below the m.p. or oxidation point of the inorg. fibers to obtain a fiber reinforced honeycomb ceramic body 1 hardly causing brittle fracture and having a large surface area.



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* NOTICES *

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2.**** shows the word which can not be translated.
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CLAIMS

[Claim(s)]
[Claim 1] The honeycomb-like fiber consolidation ceramic object which fabricates the constituent containing ceramic powder, an inorganic fiber, an inorganic substance with affinity, and the organic binder that has plasticity if needed in the shape of a honeycomb, and comes to calcinate it.
[Claim 2] The manufacture approach of the honeycomb-like fiber consolidation ceramic object characterized by calcinating at the temperature below the melting point of an inorganic fiber, or an oxidizing point after carrying out extrusion molding of the constituent containing ceramic powder, an inorganic fiber, an inorganic substance with affinity, and the organic binder that has plasticity if needed to the shape of a honeycomb and drying this extrusion-molding object.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to a honeycomb-like fiber consolidation ceramic object and its manufacture approach. It is related with the honeycomb-like fiber consolidation ceramic object which contains in more detail the ceramic powder used for adsorption material, a catalyst, catalyst support, a filter, a heater, a wallplate, a heat insulator, etc., and an inorganic fiber, and its manufacture approach.
[0002]
[Description of the Prior Art] Although a ceramic has the fault of being destroyed in brittleness when a crack once occurs and it begins to progress since toughness is inferior compared with a plastics metallurgy group ingredient etc., it is excellent in thermal resistance, reinforcement, abrasion resistance, etc., and is used as a structural material or a heat-resisting material with the gestalt of granular or a Plastic solid. As the structure with the big surface area which used such a ceramic, the ceramic honeycomb-like object attracts attention. Although pressing between heat, such as a hotpress which performs simultaneously hydrostatic molding, such as a slurry slip casting, extrusion molding, or a rubber press, and heating and shaping, etc. is common knowledge as the manufacture approach of a Plastic solid of having used the ceramic, as the manufacture approach of a honeycomb-like ceramic object, the extrusion method and the sheet laminated layers method are known, for example, the honeycomb structure object of the extrusion-molding object which carries out extrusion molding of the slurry powder of a ceramic raw material to the shape of a honeycomb, and comes to calcinate it is proposed by JP,63-242980,A. Like the honeycomb construct of the structure which carried out the laminating of the ceramic sheet proposed by JP,59-15028,B, JP,64-11808,A, etc., since a honeycomb product is obtained by drying as it is and calcinating an extrusion-molding article compared with the approach of carrying out secondary forming of the ceramic sheet which once carried out the fabricating operation to the shape of plate-like or a corrugated plate etc. to a three-dimensional network or a turning laminated structure, the honeycomb construct by this extrusion molding has the feature that a production process is very simple. However, these extrusion molding and the honeycomb construct of a sheet lamination have the brittleness which is the general property of said ceramic, and since especially the honeycomb constructs of extrusion molding are the one mold goods of a ceramic, once a crack occurs, they have the fault of being easy to produce the structure destruction which attains to the whole Plastic solid.
[0003] Although it is thought that the cause of the brittleness of a ceramic mainly originates in the crystal structure, the fiber consolidation ceramic (FRC) which combined the compound-ized technique, i.e., the ceramic powder, and fiber of the ingredient which used fiber apart from said honeycomb construct as an approach of improving the brittleness of a ceramic ingredient is known. This FRC uses as the base the compound-ized technique of the dissimilar material by the fiber currently performed as the consolidation approach of a raw material in the plastics metallurgy group ingredient. (1) The improvement in on the strength of a Plastic solid can be aimed at by making fiber pay the stress which carries out distributed combination of the fiber of high elasticity and high intensity into a ceramic base material (matrix), and is applied to a matrix, (2) Progress of the crack which the fiber distributed in the matrix produces in a Plastic solid is prevented, and fracture toughness improves by the activity of fiber, (3) The structure destruction which attains to the whole Plastic solid by developing the generated crack along with fiber can be prevented, (4) It has the features, like improvement in the high temperature strength of a Plastic solid can be aimed at by the activity of heat-resistant fiber, and is observed as a structural material excellent in high thermal resistance and the toughness possessing moderate reinforcement. Although various the manufacture approaches of FRC are proposed, it is divided roughly into a solid phase technique, a gaseous-phase method, a melting pressure process, thermal spraying, etc. according to the condition of a ceramic matrix that fiber is mixed. If it removes that a solid phase technique carries out combination use of equipment of the fiber, there is nothing, a preforming object is created with a press etc. from the shaping raw material which combined ceramic powder, fiber, an organic binder, etc. moderately beforehand, and after drying, the sintering technique of the usual solid-state powder and especially the changing place can calcinate this, can obtain FRC, and can obtain an FRC product at a simple process compared with a gaseous-phase method, a melting pressure process, thermal spraying, etc.
[0004] However, the degree of sintering of a ceramic ingredient is checked by lifting of the voidage of the Plastic solid by combination fiber etc. in FRC which carries out combination use of equipment of a ceramic ingredient and the fiber. For this reason, FRC by the solid phase technique needs a high burning temperature compared with the Plastic solid which consists only of ceramic powder, and fiber deteriorates by severe-ization of such baking conditions, and it has problems -- the merit of compound-izing is spoiled. Although heating and pressing between heat, such as a hotpress which also performs application of pressure to coincidence, are effective in relaxation of baking conditions, the configuration of mold goods is limited in the pressing between heat using a special pressing machine, and cost is also high. A melting pressure process is an approach of using ceramic ingredients comparatively fused at low temperature, such as glass, pressing fiber fit into the ceramic matrix of a melting condition, and obtaining an FRC product. However, since this approach is applicable only to the ceramic ingredient comparatively fused at low temperature, it has the problem of a raw material's being limited and the fused ceramic deteriorating fiber. A gaseous-phase method is the manufacturing technology of FRC which uses the ceramic ingredient of the gaseous state adapting CVD (chemical vacuum deposition) etc., it makes a frame the fiber which preformed, carries out the deposit sediment of the ceramic matrix to this, and obtains an FRC product. However, since this approach uses the thing of a gaseous state special as a ceramic ingredient, it has the fault in which a raw material is restrained like said melting pressure process. Moreover, in order to maintain a ceramic ingredient to a gaseous state, reduced pressure conditions are usually needed, since the deposit rate to the fiber of a ceramic is also slow, FRC by the gaseous-phase method is not fit for manufacture of the big structure, and cost is also high [FRC]. Although it was expected that general extrusion molding as the shaping approach of a ceramic had a merit great as the manufacture approach of FRC since the process is simple compared with these approaches, naturally the ceramic which added the fiber component in the ceramic industry conventionally is made inferior to a

moldability, and obtaining the ceramic mold goods which added the fiber component by extrusion molding etc. was not considered. Furthermore, carrying out extrusion molding of the Plastic solid with a complicated configuration like a honeycomb construct, and manufacturing it from a fiber content ceramic, was not taken into consideration at all.

[0005]

[Means for Solving the Problem] However, this invention persons are the approaches with the simplest extrusion molding as the manufacture approach of a honeycomb construct. Moreover, it is thought that the activity of the fiber in said FRC is useful in order to improve the brittleness of a honeycomb object. When manufacture of the fiber consolidation honeycomb object by extrusion molding is tried, the constituent containing ceramic powder, an inorganic fiber, an inorganic substance with affinity, and the organic binder that has plasticity if needed has unexpectedly good extrusion-molding nature. It succeeded in acquiring the honeycomb-like fiber consolidation ceramic object strengthened with the inorganic fiber by extrusion molding from this ceramic content constituent, and this invention was completed. Namely, the honeycomb-like fiber consolidation ceramic object which this invention fabricates the constituent containing ceramic powder, an inorganic fiber, an inorganic substance with affinity, and the organic binder that has plasticity if needed in the shape of a honeycomb, and it comes to calcinate, And extrusion molding of the constituent containing said ceramic powder and inorganic fiber, an inorganic substance with affinity, and the organic binder that has plasticity if needed is carried out to the shape of a honeycomb. After drying this extrusion-molding object, the manufacture approach of the honeycomb-like fiber consolidation ceramic object characterized by calcinating at the temperature below the melting point of an inorganic fiber or an oxidizing point is offered.

[0006] Hereafter, the honeycomb-like fiber consolidation ceramic object of this invention and its manufacture approach are explained to a detail. In the honeycomb-like fiber consolidation ceramic object of this invention, as a ceramic raw material of the ceramic content constituent component which carries out extrusion molding to the shape of a honeycomb, there is especially no limit, it can be chosen as arbitration according to the property required of a honeycomb-like fiber consolidation ceramic object product, and can use either nature or synthetic compounds. Moreover, any of an oxide system and a non-oxide system ceramic are sufficient as a ceramic raw material. If the typical thing of such a ceramic is illustrated, as an oxide system ceramic, multicomponent system oxide, such as one component system oxide, such as an alumina, a silica, a zirconia, a magnesia, and a titania, a spinel, a mullite, barium titanate, cordierite, beta-spodumene, b eucryptite, and talc, etc. can be mentioned, for example, and silica gel etc. can be used. Moreover, as a non-oxide system ceramic, silicon carbide, silicon nitride, boron carbide, boron nitride, etc. can be mentioned, and carbon materials, such as a graphite or activated carbon, can also be used. Furthermore, salts, such as the metal alkoxide which produces said oxide system ceramic and a non-oxide system ceramic by thermal decomposition etc., a chelate compound, a hydroxide, a chloride, a nitrate, and a carbonate, can also be used. The above-mentioned ceramic is independent or can also use two or more sorts together. Although such a ceramic raw material is used in this invention, the ceramic powder of the range about 0.1-20 micrometers of the mean particle diameter of whose are 0.3-10 micrometers especially is desirable.

[0007] Moderate toughness is given to a Plastic solid and the ceramic content constituent used in this invention is made to contain an inorganic fiber in order to improve the brittleness. Here, ceramic fiber metallurgy group fiber etc. can be used as an inorganic fiber, and, as for ceramic fiber, that of a non-oxide system can also use the thing of an oxide system. If the typical thing of such an inorganic fiber is illustrated, as ceramic fiber of an oxide system, glass fiber, an alumina fiber, an alumina silica fiber, a silica fiber, a potassium titanate fiber, a zirconia fiber, an alumina-BOROA silica fiber, etc. can be mentioned, for example. Moreover, as ceramic fiber of a non-oxide system, a carbon fiber, silicon carbide fiber, boron carbide fiber, boron nitride fiber, etc. can be mentioned. Moreover, stainless steel fiber, steel fiber, etc. can be illustrated as a metal fiber. These inorganic fibers are independent or can also use two or more sorts together.

[0008] It can use without limiting especially the thing currently generally used as a filler for fiber reinforced plastics (FRP) or fiber consolidation ceramics (FRC) as a carbon fiber. As an example of such a carbon fiber, a pitch based carbon fiber, a rayon system carbon fiber, a polyacrylonitrile (PAN) system carbon fiber, a meso face system carbon fiber, a vapor growth system carbon fiber, etc. can be mentioned, for example. The thing of graphite with comparatively high degree of crystallinity and the thing of carbonaceous with comparatively low degree of crystallinity can be used for these carbon fibers, and its whisker is also usable. Furthermore, what carried out the coat consolidation with other ceramics is sufficient as a SiC coat carbon fiber etc. In addition to what was illustrated above as a metal fiber, propeller-shaft-cover-ed [ceramic] group fiber, such as boron coat tungsten fiber and silicon carbide coat tungsten fiber, is also included. Although the fiber length and the diameter of fiber of an inorganic fiber change also with the classes and there is no ****** generally in this invention, as fiber length, about 0.1-20 micrometers is suitable as about 0.02-2mm and a diameter of fiber.

[0009] Moreover, although the inorganic substance which has affinity in a ceramic content constituent is made to contain, this is minded and ceramic powder and an inorganic fiber are moderately distributed and held in a Plastic solid, the organic binder which has water or plasticity if needed with an inorganic fiber is blended, and moderate extrusion-molding nature is given to a ceramic content constituent. Here, as an inorganic substance with affinity, colloidal silica, alumina sol, ethyl silicate, a silica sol, a zirconia sol, sepiolite (fibrous), clay minerals (a kaolinite, nacrite, etc.), etc. are mentioned, and the inorganic substance with these affinity can also use two or more sorts together. In these, colloidal silica and sepiolite are used preferably. Moreover, as an organic binder used by request, polyvinyl alcohol (PVA), sulfo nick methyl chloride (SMC), methyl cellulose (MC), cull BOSHIKI methyl cellulose (CMC), starch, etc. can be mentioned. In addition, decomposition clearance of these organic binder is carried out at the below-mentioned baking process. Although the content rate of each component changes with classes of ceramic powder etc. and does not generally have ****** in this invention, it is solid content conversion and is about 10 - 40 % of the weight of inorganic substances with the affinity of 30 - 87 % of the weight of ceramic powder, 0.5 - 10 % of the weight of inorganic fibers, sepiolite, or a clay mineral.

[0010] After the approach of this invention of manufacturing the above-mentioned honeycomb-like fiber consolidation ceramic object prepares the constituent containing each aforementioned component and carries out extrusion molding of this ceramic content constituent, it dries a moldings and consists of calcinating the moldings after desiccation at the temperature below the melting point of an inorganic fiber, or an oxidizing point. The approach of this invention consists of simple actuation of extrusion molding and baking fundamentally, and a process has very simple and the feature that it can perform by low cost. In this invention, as an extrusion method of a ceramic content constituent, there is especially no definition, it can put said constituent into this using the extruding press machine which has the extruding die (mouthpiece) of the configuration made necessary, and can obtain a moldings by extruding by about 20-1000cm/minute in rate preferably. Although desiccation is based on the air drying of about 24 hours in ordinary temperature, it can heat a little at about 50-100 degrees C, and it can also be dried at them. Baking is performed at the temperature below the melting point of an inorganic fiber, or an oxidizing point. Therefore, although burning temperature and firing time change with construction material of an inorganic fiber etc. and do not generally have ******, generally at least 20-minute room [about] baking conditions are adopted at the temperature of about 400-700 degrees C. If it calcinates at the temperature exceeding the melting point or the oxidizing point of an inorganic fiber, an inorganic fiber cannot attain melting or the object of this invention of deteriorating, and combination of

an inorganic fiber giving moderate toughness to a Plastic solid, and improving the brittleness.
[0011] In this way, the honeycomb-like fiber consolidation ceramic object of this invention obtained has the consolidation structure by the fiber which minded the inorganic substance in which ceramic powder and an inorganic fiber have affinity, and was distributed and held moderately, and turns into the structure with the big surface area which cannot produce the brittle fracture excellent in thermal resistance and reinforcement easily. In this invention, especially the configuration and magnitude of a honeycomb-like fiber consolidation ceramic object are not limited, but can be suitably chosen according to the purpose of use etc. In addition, in this description, the so-called hole of a cross section shall contain a polygon or a circular thing of not only a swage-block-like (6 corniform) thing but a rectangle, 3 square shapes, and others etc. with the shape of a honeycomb.
[0012]
[Example] Hereafter, this invention is further explained to a detail based on an example.
The honeycomb-like fiber consolidation ceramic object 1 of the structure which shows a perspective view was produced as follows to example 1 drawing 1 . That is, it penetrates along with the cylindrical direction of extrusion, and the honeycomb-like fiber consolidation ceramic object 1 shown in this drawing 1 has the honeycomb structure of the **** ** constituted by two or more holes 2 of the cross-section rectangle separated by the septum 3, and has the structure where fluids (a gas, liquid, etc.) circulate said hole 2 free. Therefore, this honeycomb-like fiber consolidation ceramic object 1 is useful for the gassing application which circulates a gas to said hole 2 as catalyst support for flue gas treatment in the drying agent by which a restoration activity is carried out in a dry air generator etc. or an automobile, works, etc. It faces producing the above-mentioned honeycomb-like fiber consolidation ceramic object 1 (the diameter of 5cm, height of 10cm) in this example. first -- as a ceramic raw material -- silica gel powder (a commercial item and the Mizusawa chemistry company make --) as an inorganic substance with the mean-particle-diameter of 1 micrometer 40 weight section, and affinity -- sepiolite (a commercial item --) The Mizusawa chemistry company make, the diameter of 0.01 micrometers, the fiber length of 3 micrometers 11 weight section and the colloidal silica (about 20% of solid content) 45 weight section, the carbon fiber 1 weight section, and the ceramic content constituent that comes to blend the methyl cellulose 3 weight section as organic binders which have plasticity were adjusted.
[0013] Next, the extruding press machine which has the extruding die which constituted this constituent (10kg) so that an extrusion configuration might become the cylindrical **** structure of having two or more holes 2 like drawing 1 was supplied, and extrusion molding was carried out by part for extrusion rate/of 200cm. Stoving of this moldings was carried out with microwave. Next, after putting this moldings all over a firing furnace (electric furnace), temperature up was carried out to the temperature of 500 degrees C by part for programming-rate/of 2 degrees C, and at this temperature, it held for 1 hour and calcinated. Then, it cooled to the room temperature, stopping the energization to a firing furnace and leaving a moldings all over a furnace, and the honeycomb-like fiber consolidation ceramic object 1 of this invention like instantiation was acquired to drawing 1 . This ceramic object was distributed and held at homogeneity at the sepiolite and colloidal silica of silica gel powder and the inorganic substance in which a carbon fiber has affinity, and was what cannot produce a brittle fracture with reinforcement sufficient as the structure easily.
[0014] The honeycomb-like fiber consolidation ceramic object of this invention was acquired like the example 1 except having used example 2 ceramic powder as alumina powder (a commercial item, mean particle diameter of 1 micrometer). This ceramic object was what cannot produce a brittle fracture with reinforcement sufficient as the structure easily like the honeycomb-like fiber consolidation ceramic object of an example 1.
[0015] In addition, although the configuration of a honeycomb-like fiber consolidation ceramic object is used as the cylinder in each above-mentioned example In this invention, especially the configuration of a honeycomb-like fiber consolidation ceramic object is not limited to drawing 1 by the cylinder of instantiation. for example, like the honeycomb-like fiber consolidation ceramic object 4 which has the honeycomb structure of the **** ** constituted by two or more holes 5 penetrated along with the direction of extrusion of a prism as shown in drawing 2 According to the purpose of using a honeycomb-like fiber consolidation ceramic object etc., various configurations, such as a cylinder, a prism, or an elliptic cylinder, can be chosen suitably.
[0016]
[Effect of the Invention] This invention offered a honeycomb-like fiber consolidation ceramic object and its manufacture approach, and it became possible to offer a honeycomb-like fiber consolidation ceramic object with the big surface area which cannot produce easily the brittle fracture which was excellent in thermal resistance and reinforcement by the simple approach of extrusion molding, and was strengthened with the inorganic fiber according to this invention as stated above. Such a honeycomb-like fiber consolidation ceramic object of this invention can be used effectively as adsorption material, a catalyst, catalyst support, a filter, a heater, a wallplate, a heat insulator, etc.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the perspective view showing the outline of the honeycomb-like fiber consolidation ceramic object concerning the example of this invention.
[Drawing 2] It is the perspective view showing the outline of other examples of the honeycomb-like fiber consolidation ceramic object of this invention.
[Description of Notations]
1 Honeycomb-like Fiber Consolidation Ceramic Object
2 Hole
3 Septum
4 Honeycomb-like Fiber Consolidation Ceramic Object
5 Hole

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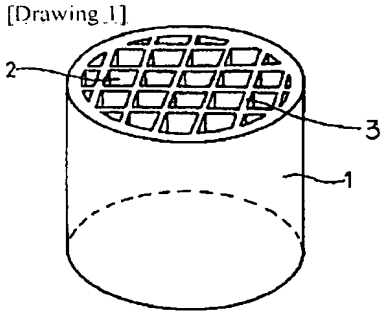
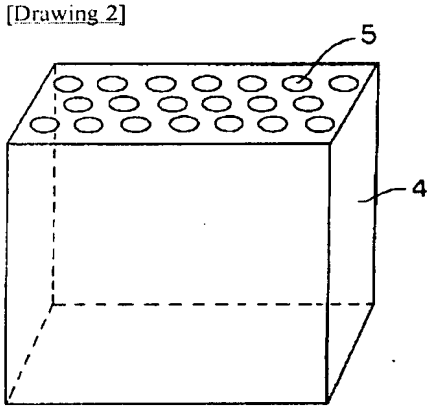
DRAWINGS

[Drawing 1]



[Drawing 2]



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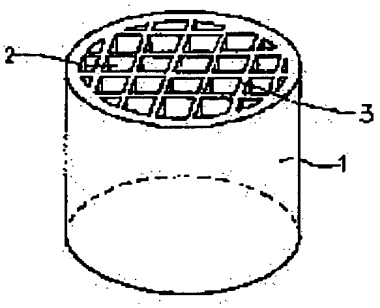
CONSTITUTION: Ceramic powder such as alumina, spinel or silicon carbide powder, inorg. fibers such as ceramic, metal or carbon fibers and an inorg. substance having binding property such as colloidal silica, sepiolite or an alumina sol are prepd. and a ceramic-contg. compsn. is obtd. by using these starting materials or further using an org. binder such as PVA or methylcellulose. This compsn. having satisfactory extrusion moldability is extrusion-molded into a honeycomb shape with holes 2 having a square cross section formed by partition walls 3. The resulting molding is dried and fired at a temp. below the m.p. or oxidation point of the inorg. fibers to obtain a fiber reinforced honeycomb ceramic body 1 hardly causing brittle fracture and having a large surface area.



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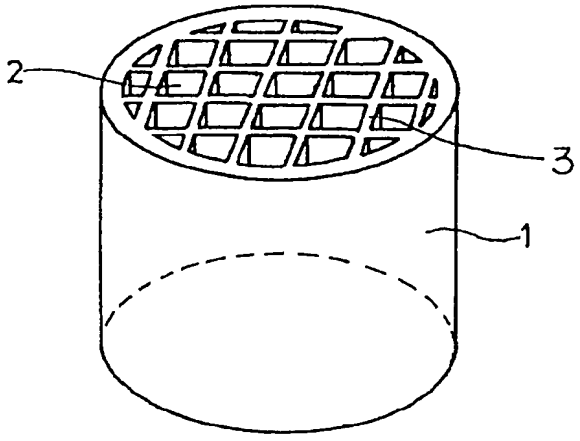
(71)出願人　000129183
株式会社カワタ
大阪府大阪市西区阿波座１丁目15番15号
(71)出願人　000205627
大阪府
大阪府大阪市中央区大手前２丁目１番22号
(72)発明者　宮本　大樹
奈良県奈良市西千代ヶ丘１丁目23番17号
(72)発明者　太田　道之助
大阪府堺市庭代台１丁目４番４号
(74)代理人　弁理士　大家　邦久

最終頁に続く

(54)【発明の名称】　ハニカム状繊維強化セラミック体およびその製造方法

(57)【要約】
【目的】　無機繊維により強化されたハニカム状繊維強化セラミック体およびその製造方法を提供する。
【構成】　セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物をハニカム状に成形し焼成してなるハニカム状繊維強化セラミック体であり、前記の各成分を含有する組成物をハニカム状に押出成形し、乾燥した後、無機繊維の融点もしくは酸化点以下の温度で焼成して製造する。



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【特許請求の範囲】

【請求項１】　セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物をハニカム状に成形し焼成してなるハニカム状繊維強化セラミック体。

【請求項２】　セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物をハニカム状に押出成形し、この押出成形物を乾燥した後、無機繊維の融点もしくは酸化点以下の温度で焼成することを特徴とするハニカム状繊維強化セラミック体の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明はハニカム状繊維強化セラミック体およびその製造方法に関する。より詳しくは、吸着材、触媒、触媒担体、フィルター、ヒーター、壁材、断熱材などに使用されるセラミック粉末と無機繊維とを含有するハニカム状繊維強化セラミック体およびその製造方法に関するものである。

【０００２】

【従来の技術およびその課題】セラミックはプラスチックや金属材料などに比べて靭性が劣るために、一旦亀裂が発生して進展し始めると脆性的に破壊されてしまうという欠点を有するが、耐熱性、強度、耐摩耗性などに優れており、粒状あるいは成形体などの形態で構造材料や耐熱材料として使用されている。このようなセラミックを使用した表面積の大きな構造体として、ハニカム状のセラミック体が注目されている。セラミックを利用した成形体の製造方法としては、泥漿鋳込み成形、押出成形、あるいはラバープレスなどの静水圧成形や、加熱と成形を同時に行なうホットプレスなどの熱間加圧成形等が周知であるが、ハニカム状セラミック体の製造方法としては押出成形法およびシート積層法が知られており、例えば特開昭63-242980 号公報にはセラミック原料のスラリー粉末をハニカム状に押出成形し焼成してなる押出成形物のハニカム構造体が提案されている。この押出成形によるハニカム構成体は、特公昭59-15028号公報および特開昭64-11808号公報等に提案されているセラミックシートを積層した構造のハニカム構成体のように、平板状あるいは波板状等に一旦成形加工したセラミックシートを三次元網目構造や旋回積層構造に二次成形する方法と比べて、押出成形品をそのまま乾燥して焼成することによりハニカム製品が得られることから製造工程が極めて簡便であるという特色を有する。しかし、これら押出成形およびシート積層のハニカム構成体は前記セラミックの一般的性質である脆さを有しており、特に押出成形のハニカム構成体はセラミックの一体成形品であることから、亀裂が一旦発生すると成形体全体に及ぶ構造破壊が生じ易いという欠点がある。

【０００３】セラミックの脆さの原因は主にその結晶構造に由来すると考えられているが、セラミック材料の脆さを改善する方法として、前記ハニカム構成体とは別に繊維を使用した材料の複合化技術、すなわちセラミック粉末と繊維とを組合せた繊維強化セラミック（ＦＲＣ）が知られている。このＦＲＣはプラスチックや金属材料において素材の強化方法として行なわれている繊維による異種材料の複合化技術をベースとしたものであり、(1) セラミック母材（マトリックス）中に高弾性、高強度の繊維を分散配合し、マトリックスにかかる応力を繊維に負担させることにより成形体の強度向上がはかれること、(2) マトリックス中に分散した繊維が成形体に生じる亀裂の進展を阻止し、また繊維の使用により破壊靭性が向上すること、(3) 発生した亀裂を繊維に沿って進展させることにより成形体全体に及ぶ構造破壊を防止できること、(4) 耐熱繊維の使用により成形体の高温強度の向上がはかれること、等の特色を有しており、高耐熱性と適度な強度を具備した靭性に優れた構造材料として注目されている。ＦＲＣの製造方法は種々提案されているが、繊維が混入されるセラミックマトリックスの状態により、固相法、気相法、溶融圧入法、溶射等に大別される。固相法は繊維を組合せ使用することを除けば通常の固体粉末の焼結技法と特に変るところはなく、予めセラミック粉末と繊維と有機結合剤などを適度に組合せた成形原料からプレス等により予備成形体を作成し、乾燥した後、これを焼成してＦＲＣを得るものであり、気相法、溶融圧入法、溶射等に比べて簡便な工程でＦＲＣ製品を得ることができる。

【０００４】しかし、セラミック材料と繊維とを組合せ使用するＦＲＣにおいては配合繊維による成形体の空隙率の上昇などにより、セラミック材料の焼結性が阻害される。このため固相法によるＦＲＣはセラミック粉末のみからなる成形体に比べて高い焼成温度を必要とし、このような焼成条件の過酷化により繊維が変質して複合化のメリットが損なわれる等の問題がある。焼成条件の緩和には加熱と同時に加圧も行なうホットプレスなどの熱間加圧成形が有効であるが、特殊な加圧成形機を用いる熱間加圧成形では成形品の形状が限定されるし、コストも高い。溶融圧入法はガラスなどの比較的低温度で溶融するセラミック材料を使用し、溶融状態のセラミックマトリックス中に繊維を圧入してＦＲＣ製品を得る方法である。しかし、この方法は比較的低温度で溶融するセラミック材料にしか適用できないので原料が限定されること、また溶融したセラミックが繊維を変質させる等の問題がある。気相法はＣＶＤ（化学蒸着）等を応用した気体状態のセラミック材料を使用するＦＲＣの製造技術であり、予備成形した繊維を骨格にして、これにセラミックマトリックスを析出沈積させてＦＲＣ製品を得るものである。しかし、この方法はセラミック材料として特殊な気体状態のものを使用することから、前記溶融圧入法と同様に原料が制約される欠点がある。また、セラミッ

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ク材料を気体状態に維持するためには通常減圧条件を必要とし、セラミックの繊維に対する析出速度も遅いことから、気相法によるＦＲＣは大きな構造体の製造には向かないし、コストも高い。これら方法に比べてセラミックの成形方法として一般的な押出成形は工程が簡便であることから、ＦＲＣの製造方法として多大なメリットがあると予想されるが、従来セラミック業界においては繊維成分を添加したセラミックは成形性に劣るのが当然のこととされており、繊維成分を添加したセラミック成形品を押出成形により得るなどということは考えられていなかった。まして、ハニカム構成体のような形状の複雑な成形体を繊維含有セラミックから押出成形して製造することは全く考慮されていなかった。

【０００５】

【課題を解決するための手段】しかし、本発明者らはハニカム構成体の製造方法として押出成形が最も簡便な方法であり、またハニカム体の脆さを改善するためには前記ＦＲＣにおける繊維の使用が有用であると考え、押出成形による繊維強化ハニカム体の製造を試みたところ、セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物が予想外に良好な押出成形性を有しており、このセラミック含有組成物から押出成形により無機繊維で強化されたハニカム状繊維強化セラミック体を得ることに成功し、本発明を完成した。すなわち、本発明は、セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物をハニカム状に成形し焼成してなるハニカム状繊維強化セラミック体、および前記セラミック粉末と無機繊維と結合性を持つ無機物と必要に応じて可塑性を有する有機結合剤とを含有する組成物をハニカム状に押出成形し、この押出成形物を乾燥した後、無機繊維の融点もしくは酸化点以下の温度で焼成することを特徴とするハニカム状繊維強化セラミック体の製造方法を提供したものである。

【０００６】以下、本発明のハニカム状繊維強化セラミック体、およびその製造方法を詳細に説明する。本発明のハニカム状繊維強化セラミック体において、ハニカム状に押出成形するセラミック含有組成物成分のセラミック原料としては特に制限はなく、ハニカム状繊維強化セラミック体製品に要求される特性などに応じて任意に選択することができ、天然あるいは合成品のいずれをも使用できる。またセラミック原料は酸化物系および非酸化物系セラミックのいずれでもよい。このようなセラミックの代表的なものを例示すると、酸化物系セラミックとしては、例えばアルミナ、シリカ、ジルコニア、マグネシア、チタニアなどの一成分系酸化物、スピネル、ムライト、チタン酸バリウム、コージェライト、β－スポジューメン、β－ユークリプタイト、タルクなどの多成分系酸化物などを挙げることができ、シリカゲルなども用いることができる。また、非酸化物系セラミックとしては、炭化ケイ素、窒化ケイ素、炭化ホウ素、窒化ホウ素などを挙げることができ、黒鉛あるいは活性炭などの炭素材料も用いることができる。さらには、加熱分解等により前記酸化物系セラミックや非酸化物系セラミックを生じる金属アルコキシド、キレート化合物、水酸化物、塩化物、硝酸塩、炭酸塩などの塩類も使用することができる。上記のセラミックは単独で、あるいは２種以上を併用することもできる。本発明ではこのようなセラミック原料を使用するが、その平均粒径が0.1 ～２０μｍ程度、特に0.3 ～１０μｍの範囲のセラミック粉末が好ましい。

【０００７】本発明において用いるセラミック含有組成物には、成形体に適度の靭性を付与し、その脆さを改善する目的で無機繊維を含有させる。ここで、無機繊維としてはセラミック繊維や金属繊維などを用いることができ、セラミック繊維は酸化物系のものも、非酸化物系のも使用できる。このような無機繊維の代表的なものを例示すると、酸化物系のセラミック繊維としては、例えばガラスファイバー、アルミナ繊維、アルミナ・シリカ繊維、シリカ繊維、チタン酸カリウム繊維、ジルコニア繊維、アルミナーボロア・シリカ繊維等を挙げることができる。また非酸化物系のセラミック繊維としては、炭素繊維、炭化ケイ素繊維、炭化ホウ素繊維、窒化ホウ素繊維等を挙げることができる。また金属繊維としては、ステンレス鋼繊維、スチール繊維等を例示することができる。これら無機繊維は単独で、あるいは２種以上を併用することもできる。

【０００８】炭素繊維としては、繊維強化プラスチック（ＦＲＰ）や繊維強化セラミック（ＦＲＣ）用の充填材として一般的に使用されているものを特に限定することなく利用できる。そのような炭素繊維の具体例としては、例えば、ピッチ系炭素繊維、レーヨン系炭素繊維、ポリアクリロニトリル（ＰＡＮ）系炭素繊維、メソフェース系炭素繊維および気相成長系炭素繊維等を挙げることができる。これら炭素繊維は、結晶化度が比較的高い黒鉛質のものも、結晶化度が比較的低い炭素質のものも使用でき、ウィスカーも使用可能である。さらには、ＳｉＣ被覆炭素繊維など、他のセラミックで被覆強化したものでもよい。金属繊維としては上記に例示したもの以外に、ホウ素被覆タングステン繊維や炭化ケイ素被覆タングステン繊維などのセラミック被覆金属繊維も含む。本発明において無機繊維の繊維長および繊維径は、その種類によっても異なり一概には言えないが、繊維長としては0.02～２㎜程度、繊維径としては0.1 ～２０μｍ程度が適当である。

【０００９】またセラミック含有組成物には結合性を持つ無機物を含有させ、これを介してセラミック粉末と無機繊維とを成形体中に適度に分散、保持するが、無機繊維とともに必要に応じて水あるいは可塑性を有する有機結合剤などを配合し、セラミック含有組成物に適度な押

出成形性を付与する。ここで、結合性を持つ無機物としてはコロイダルシリカ、アルミナゾル、エチルシリケート、シリカゾル、ジルコニアゾル、セピオライト（繊維状）、粘土鉱物（カオリナイト、ナクライト等）などが挙げられ、これら結合性を持つ無機物は２種以上を併用することもできる。これらの中ではコロイダルシリカ、セピオライトが好ましく用いられる。また所望により使用される有機結合剤としては、ポリビニルアルコール（ＰＶＡ）、スルホニックメチルクロライド（ＳＭＣ）、メチルセルロース（ＭＣ）、カルボシキメチルセルロース（ＣＭＣ）、デンプン等を挙げることができる。なお、これら有機結合剤は後述の焼成工程で分解除去される。本発明において各成分の含有割合はセラミック粉末の種類等によっても異なり一概には言えないが、固形分換算で、セラミック粉末３０～８７重量%、無機繊維0.5 ～１０重量%、セピオライトあるいは粘土鉱物等の結合性を持つ無機物１０～４０重量%程度である。

【００１０】上記のハニカム状繊維強化セラミック体を製造する本発明の方法は、前記の各成分を含有する組成物を調製し、このセラミック含有組成物を押出成形した後、成形物を乾燥し、乾燥後の成形物を無機繊維の融点もしくは酸化点以下の温度で焼成するすることからなる。本発明の方法は基本的に押出成形および焼成という簡便な操作からなるものであり、工程が極めて簡易かつ低コストで実行できるという特色を有する。本発明においてセラミック含有組成物の押出成形法としては特に限定はなく、所要とする形状の押出ダイ（口金）を有する押出成形機を用い、これに前記組成物を入れ、好ましくは２０～1000cm／分程度の速度で押出すことにより成形物を得ることができる。乾燥は常温にて２４時間程度の自然乾燥によるが、５０～１００℃程度に若干加熱して乾燥することもできる。焼成は無機繊維の融点もしくは酸化点以下の温度で行なう。従って、焼成温度および焼成時間は無機繊維の材質等によって異なり一概には言えないが、一般的には４００～７００℃程度の温度で少なくとも２０分間程度の焼成条件が採用される。無機繊維の融点もしくは酸化点を越える温度で焼成を行なうと無機繊維が溶融もしくは変質してしまい、無機繊維の配合により成形体に適度の靭性を付与し、その脆さを改善するという本発明の目的を達成できない。

【００１１】こうして得られる本発明のハニカム状繊維強化セラミック体は、セラミック粉末と無機繊維とが結合性を持つ無機物を介して適度に分散、保持された繊維による強化構造を有し、耐熱性および強度に優れた脆性破壊を生じにくい表面積の大きな構造体となる。本発明においてハニカム状繊維強化セラミック体の形状および大きさは特に限定されず、使用目的等に応じて適宜選択することができる。なお、本明細書においてハニカム状とは、いわゆる断面の穴がはちの巣状（６角状）のものだけでなく、方形、３角形その他の多角形あるいは円形

のものなどを含むものとする。

【００１２】

【実施例】以下、実施例をもとに本発明をさらに詳細に説明する。

実施例１

図１に斜視図を示す構造のハニカム状繊維強化セラミック体１を以下のようにして作製した。すなわち、この図１に示すハニカム状繊維強化セラミック体１は、円柱の押出方向に沿って貫通し、隔壁３によって隔てられる断面方形の複数の穴部２により構成されるごばん目状のハニカム構造を有し、前記穴部２を流体（気体や液体など）が自在に流通する構造となっている。従って、このハニカム状繊維強化セラミック体１は乾燥空気発生装置等において充填使用される乾燥剤、あるいは自動車や工場等における排ガス処理用の触媒担体などとして、前記穴部２に気体を流通させるガス処理用途などに有用である。本例では上記ハニカム状繊維強化セラミック体１（直径５cm、高さ１０cm）を作製するに際し、まず、セラミック原料としてシリカゲル粉末（市販品、水澤化学社製、平均粒径１μｍ）４０重量部、結合性を持つ無機物としてセピオライト（市販品、水澤化学社製、直径0.01μｍ、繊維長３μｍ）１１重量部およびコロイダルシリカ（固形分約２０%）４５重量部、炭素繊維１重量部、可塑性を有する有機結合剤としてメチルセルロース３重量部を配合してなるセラミック含有組成物を調整した。

【００１３】次にこの組成物（１０kg）を押出形状が図１のような複数の穴部２を有する円柱のごばん目構造になるように構成した押出ダイを有する押出成形機に供給し、押出速度２００cm／分で押出成形した。この成形物をマイクロ波にて加熱乾燥させた。次にこの成形物を焼成炉（電気炉）中に静置した後、昇温速度２℃／分で５００℃の温度まで昇温し、この温度で１時間保持して焼成した。その後、焼成炉への通電を停止して成形物を炉中に放置したまま室温まで冷却し、図１に例示の如き本発明のハニカム状繊維強化セラミック体１を得た。このセラミック体はシリカゲル粉末と炭素繊維が結合性を持つ無機物のセピオライトおよびコロイダルシリカに均一に分散、保持されており、構造体として十分な強度を有した脆性破壊を生じにくいものであった。

【００１４】実施例２

セラミック粉末をアルミナ粉（市販品、平均粒径１μｍ）としたこと以外は実施例１と同様にして本発明のハニカム状繊維強化セラミック体を得た。このセラミック体は実施例１のハニカム状繊維強化セラミック体と同様に構造体として十分な強度を有した脆性破壊を生じにくいものであった。

【００１５】なお、上記の各実施例においてはハニカム状繊維強化セラミック体の形状を円柱としているが、本発明においてハニカム状繊維強化セラミック体の形状は

図１に例示の円柱に特に限定されず、例えば図２に示されるような角柱の押出方向に沿って貫通する複数の穴部５によって構成されるごばん目状のハニカム構造を有するハニカム状繊維強化セラミック体４の如く、ハニカム状繊維強化セラミック体の使用目的などに応じて円柱、角柱あるいは楕円柱等の種々の形状を適宜選択し得るものである。

【００１６】

【発明の効果】以上述べたとおり、本発明はハニカム状繊維強化セラミック体およびその製造方法を提供したものであり、本発明によれば押出成形という簡便な方法により、耐熱性および強度に優れ、無機繊維で強化された脆性破壊を生じにくい表面積の大きなハニカム状繊維強化セラミック体を提供することが可能になった。このような本発明のハニカム状繊維強化セラミック体は、吸着材、触媒、触媒担体、フィルター、ヒーター、壁材、断熱材等として有効利用できる。

【図面の簡単な説明】

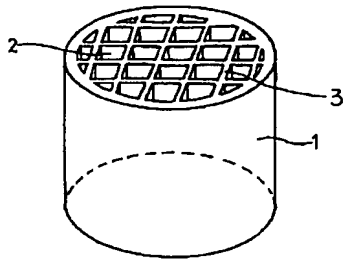
【図１】本発明の実施例に係るハニカム状繊維強化セラミック体の概要を示す斜視図である。

【図２】本発明のハニカム状繊維強化セラミック体の他の例の概要を示す斜視図である。

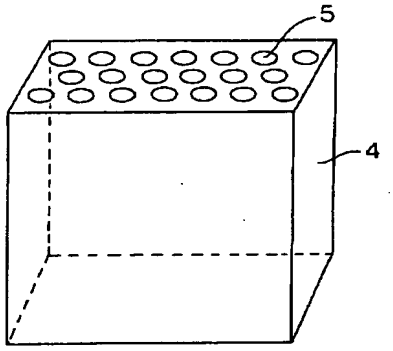
【符号の説明】

１　ハニカム状繊維強化セラミック体
２　穴部
３　隔壁
４　ハニカム状繊維強化セラミック体
５　穴部

【図１】



【図２】



フロントページの続き

(72)発明者　石川　敢三
兵庫県三田市あかしあ台５丁目30番地２
あかしあ台ハイツ第２　３棟206号

(72)発明者　助田　義彦
兵庫県宝塚市安倉南４丁目13番43号　フレグランス宝塚105号

(72)発明者　鍛示　恭斉
兵庫県宝塚市大吹町３番11号　丸美苑203号